Gallium arsenide p-i-n radial structures for photovoltaic applications

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Gallium arsenide p-i-n radial junctions were fabricated by molecular beam epitaxy. The current-voltage characteristics of single nanowires were measured in the dark and under various illumination conditions including 1.5 AM. The total efficiency was 4.5%. Spatially resolved and power dependent photocurrent measurements indicate that the p-i-n junction is homogeneous along the nanowire. Electroluminescence measurements show an emission peak at about 1,4 eV, further corroborating the good quality of the nanowire. These results constitute an important progress for the use of nanowires in photovoltaic applications.

Third generation solar cells represent alternatives to traditional bulk and thin film devices. They constitute a novel way to improve the ratio between photovoltaic efficiency and total cost, by including new physical principles and solutions offered from nanotechnology.[1,2] Semiconductor nanowires are expected to play an important role as components of third generation solar cells.[3] Particular attention has been given to core-shell radial p-i-n structures, in which the direction of light absorption is orthogonal to the carrier collection. It is predicted that such structures enable an extremely efficient carrier collection, as the minority carrier diffusion length can in all cases be shorter than the optical absorption length.[4] This relaxes the demand for the material quality, which at the same time can lead to the reduction of the fabrication costs. Supplementary advantages in using nanowires for photovoltaic applications are the improvement in the light collection and the minimization of the amount of material used.[5] Moreover, it is known that lattice mismatched materials can be integrated when grown in the form of nanowires. This enables both the formation of strain-free multijunction solar cells and the utilization of any substrate. [6,7]

Molecular beam epitaxy (MBE) grown GaAs nanowires are especially suitable for the fabrication of nanowire solar cells. From one side, MBE is a versatile technique. Axial and radial growth can be switched at convenience. Layers grown on the radial direction can be obtained with atomic precision and perfect epitaxial relation.[8] The quality of the obtained interface is MBE-grade, which is an essential point for the fabrication of an efficient solar cell. Additionally, GaAs nanowires can be obtained without the use of gold, which is generally an unwanted impurity in the semiconductor industry.[9,10] Growth occurs up to 15 times faster than thin film growth, which is a further advantage for industrial applications.[11] Finally, GaAs is the semiconductor whose absorption is best matched with the solar spectrum.[12]

The GaAs p-i-n nanowire structures were synthesized in a Gen II MBE system. Two-inch (111)B GaAs wafers coated with a sputtered 10 nm thick silicon dioxide were used as substrates. The nanowire growth was carried out at a nominal GaAs growth rate of 0.25 Å/s, As_4 partial pressure of $2x10^{-6}$ mbar (Ga rich conditions), a temperature of 630 °C and with 7 rpm rotation. As we have previously shown, the nanowires grown on coated (111)B GaAs wafers were perpendicular to the substrate surface. The core of the p-i-n nanowire junction was doped type p. This was achieved by adding a silicon flux during the

nanowire growth. For that, the silicon cell was heated with 13 Amp, which corresponds to a doping flux of ~$2x10^{10}$ at.cm^{-2}, leading to a concentration of ~$2x10^{18}$ cm^{-3} for a growth rate of 1 Å/s. Silicon is an amphoteric impurity in GaAs. This means that the incorporation of silicon can lead to n or p type doping, depending on whether it is incorporated in As or Ga sites.[13] In the case of gallium-assisted GaAs nanowire growth, we have observed that the incorporation of Si in the growth results in a p-type doping. More detailed studies on the doping of this type of nanowires will be published in a near future.

After 3 h of growth, the nanowires presented a total length of 9 μm. Then, the growth was stopped and the conditions were changed towards planar MBE growth. The As_4 partial pressure was increased to $5x10^{-5}$ mbar, which resulted in the crystallization of the Ga droplet. The fabrication of the p-i-n junction continued by the epitaxy of an intrinsic (i) and a n-type layer on the facets of the nanowires. For this purpose, the As_4 beam flux was kept at $5x10^{-5}$ mbar and the temperature lowered to 465°C. The Ga flux was also increased to 2 Å/s. These conditions had previously been shown to be the ideal for growth on {110} nanofacets.[14] We have shown in previous works that these growth conditions lead to homogeneous layers on all the nanowire facets. The intrinsic layer grown directly on the nanowire core had a thickness of 15 nm. It was followed by a n-type external layer of about 50 nm. The n-type doping was obtained by adding silicon during growth. This should lead to a doping density of 10^{18} cm^{-3}. For this growth conditions, due to the lower temperature and higher As_4 beam flux, the incorporation of Si leads to a n-type layer.[15]

The p-i-n nanowire structures were transferred on an oxidized silicon substrate. The nanowires were first diluted in isopropanol by dipping a piece of substrate in a soft ultrasonic bath during 30 s. By shortly soaking the device substrate on the solution, nanowires sparsely dispersed on the surface could be found. The contacting process was realized with optical lithography. 9 μm long nanowires can be easily observed with the optical objective of the mask aligner, making the alignment with the contact mask possible. The p-type core of the nanowire was contacted by first etching a section of the n-type and intrinsic layers of the nanowire. The etching was performed with a citric acid solution, whose etching rate had been calibrated before. After that, a Pd/Ti/Au (70/10/120 nm) layer was evaporated to form an ohmic contact

with the p-type core. A second lithographic step was realized with the purpose of contacting the n-type shell. For this, we used a Ti/Au (10/240 nm) layer. A sketch of the contacted p-i-n nanowire structure is presented in Fig.1a. There the three coaxial layers can be observed, as well as the contacting of the inner and exterior layer. A Scanning Electron Micrograph of a real structure is shown in Fig. 1b. The microscopic contacts shown there were used for the measurement of the electrical response in the dark and under illumination.

The current-voltage characteristic of the contacted p-i-n nanowires were measured in the dark, under various illumination conditions including 1.5 AM. Typical I-V characteristics in the dark and under illumination are shown in Fig. 2a. A typical diode behavior was measured. Upon illumination, an increase in the photocurrent was observed. The current-voltage characteristics were first measured as a function of the illumination intensity at room temperature. The nanowire was illuminated with a diode laser with excitation wavelength of 780 ± 10 nm. In order to cover the whole nanowire the incident beam was focused to a spot of approximately 15 μm. The relation between the generated photocurrent and the excitation is shown in Fig. 2a and b. From 1 μW to 189 μW, we observed a linear relation in log-log scale between the photocurrent and the excitation power. The linear relation between the photocurrent and the illumination intensity is typical of a direct semiconductor material of good quality. The efficiency of the nanowire device was measured under 1.5 AM illumination conditions. The total efficiency was calculated by dividing the maximum generated power density by the total incident energy density at 1.5 AM. The total area considered was the projected area of the p-i-n junction. It was measured by scanning electron micrograph and corresponds to the product of length L and diameter of the nanowire in the p-i-n region. For clarity, we have indicated L in Fig. 1b. For the best sample a value of 4.5% was obtained. The fill factor was 0.65. This is to date, the best result obtained in a solid state nanowire solar cell.[16,17,18,19]

In order to get more insight in the functioning of the nanowire p-i-n junction, spatially resolved photocurrent measurements were realized. The contacted nanowires were mounted on an x-y piezostage of a confocal microscope. The confocal lens of the microscope was used to illuminate the nanowire with a spot of about 1 μm in diameter. The short circuit current was mapped scanning the area around the

nanowire in grid every 250 nm. The image obtained superimposed to the SEM picture of the same area is shown in Fig.3a. When the illumination spot is located on the uncovered p-type region, no photocurrent is observed. An increase in the photocurrent is only observed when the p-i-n junction is illuminated. The response is homogeneous along the wire, in agreement with the existence of a homogeneous deposition of the intrinsic and n-type layers on the nanowire facets.

In order to further characterize the p-i-n junction, the light emitted by the nanowire in forward bias was measured. This corresponds to the regime in which the junction works as a light emitting diode. A typical spectrum is shown in Fig. 3b. The emission peak at 1.42 eV is in good agreement with the room temperature band gap of GaAs. The existence of electroluminescence at room temperature constitutes a further proof of the quality of the nanowires and the p-i-n junction.

As a conclusion, we have presented results on p-i-n radial junctions of GaAs nanowires. The versatility of MBE allows for the in situ preparation of the junctions and for good quality of the interfaces and the material, as it has been shown by the current-voltage and spatial resolved photocurrent characteristics. The achieved efficiency and fill factor of respectively 4.5% and 0.65 under 1.5 AM illumination are to our knowledge the best reported results in radial nanowire solar cells. This work represents a good progress for the use of semiconductor nanowires in the fabrication of third generation solar cells.

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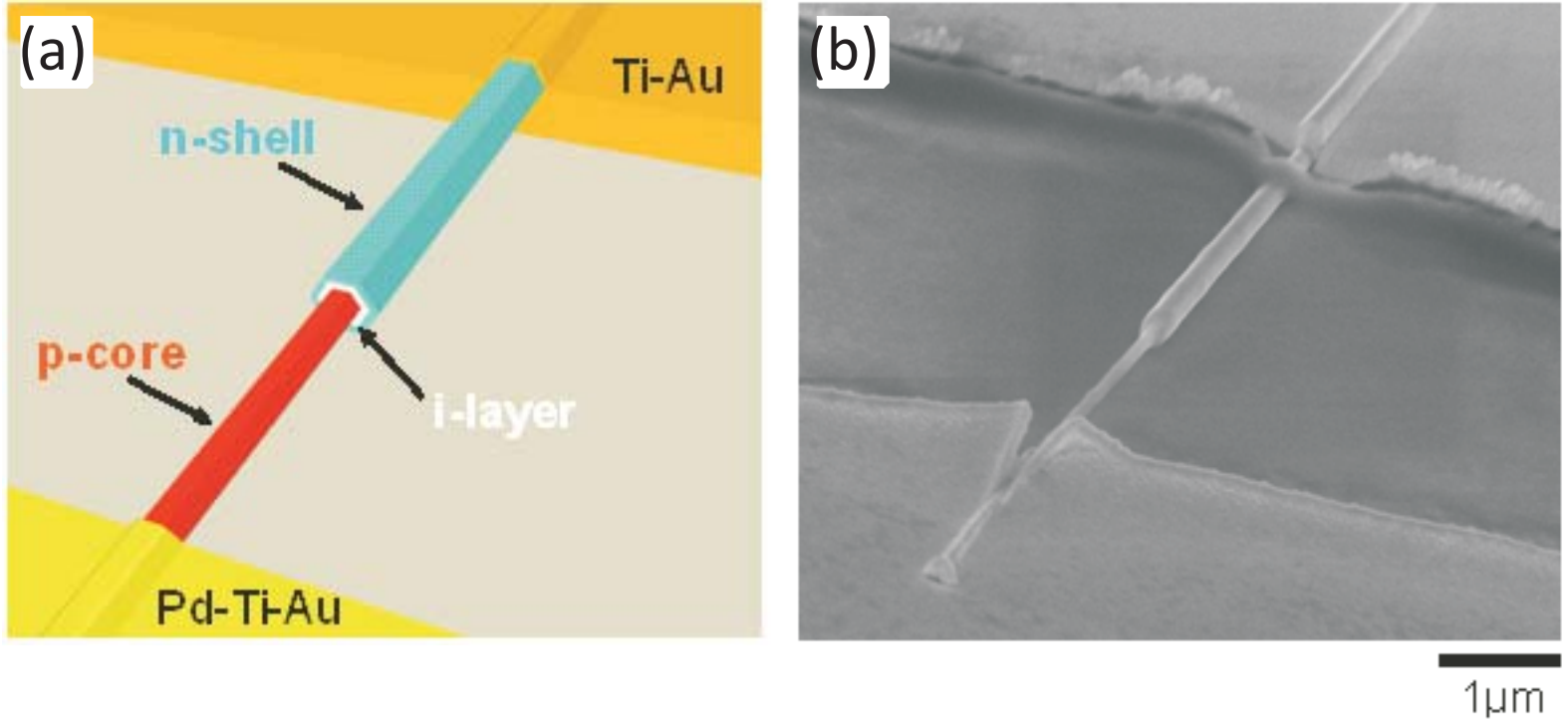
Figure captions:

Figure 1. (a) Sketched of the device structure (b) Scanning Electron Micrograph of a typical device

Figure 2 (a) Current-voltage measurements of a nanowire p-i-n junction in the dark and under various illumination powers from 1 to 200 μW. (b) Zero voltage photocurrent as a function of the illumination power, corresponding to the measurements in (a).

Figure 3. (a) Mapping of the photocurrent in the nanowire p-i-n junction (b) optical emission of the p-i-n junction in forward bias (light emitting diode mode)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p-core
i-layer
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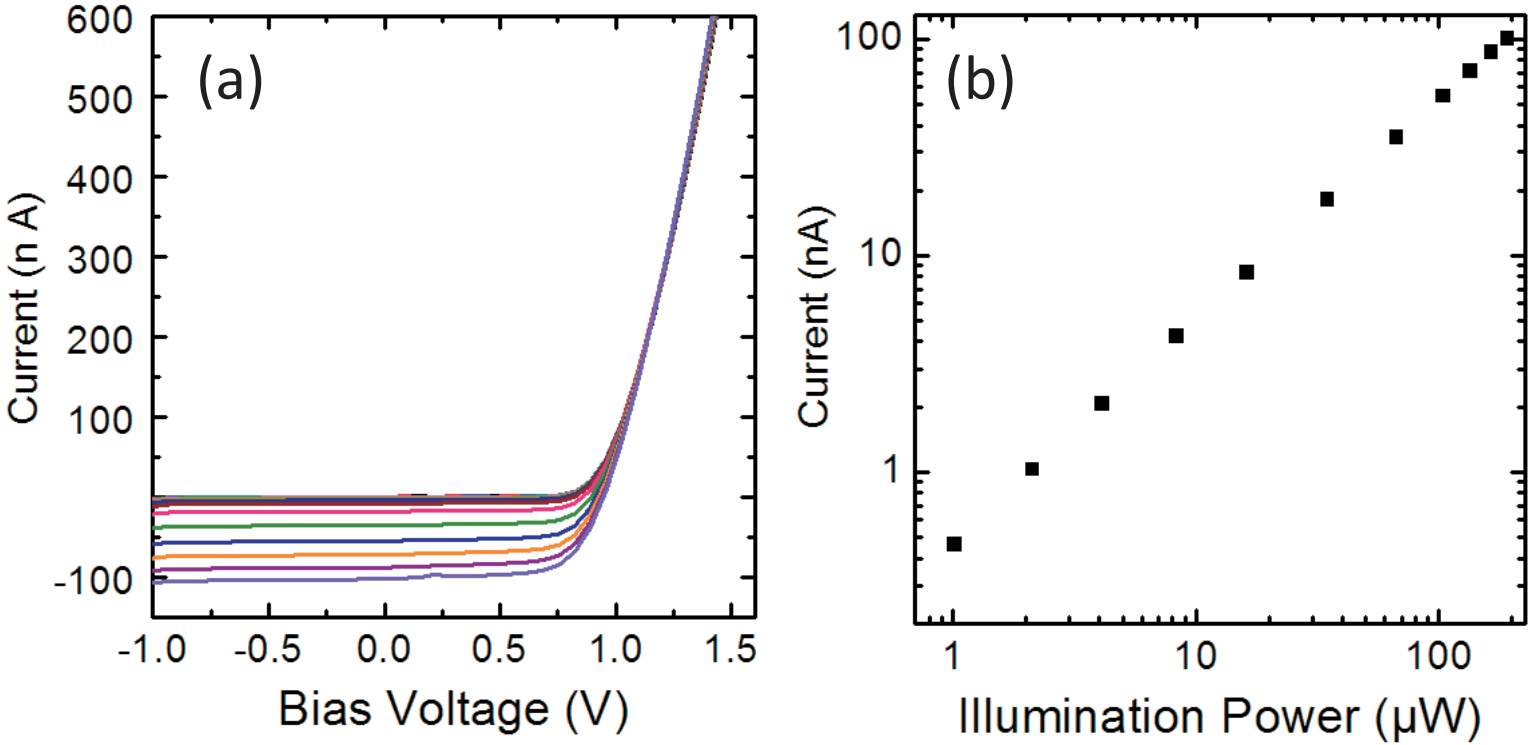
(b)
1μm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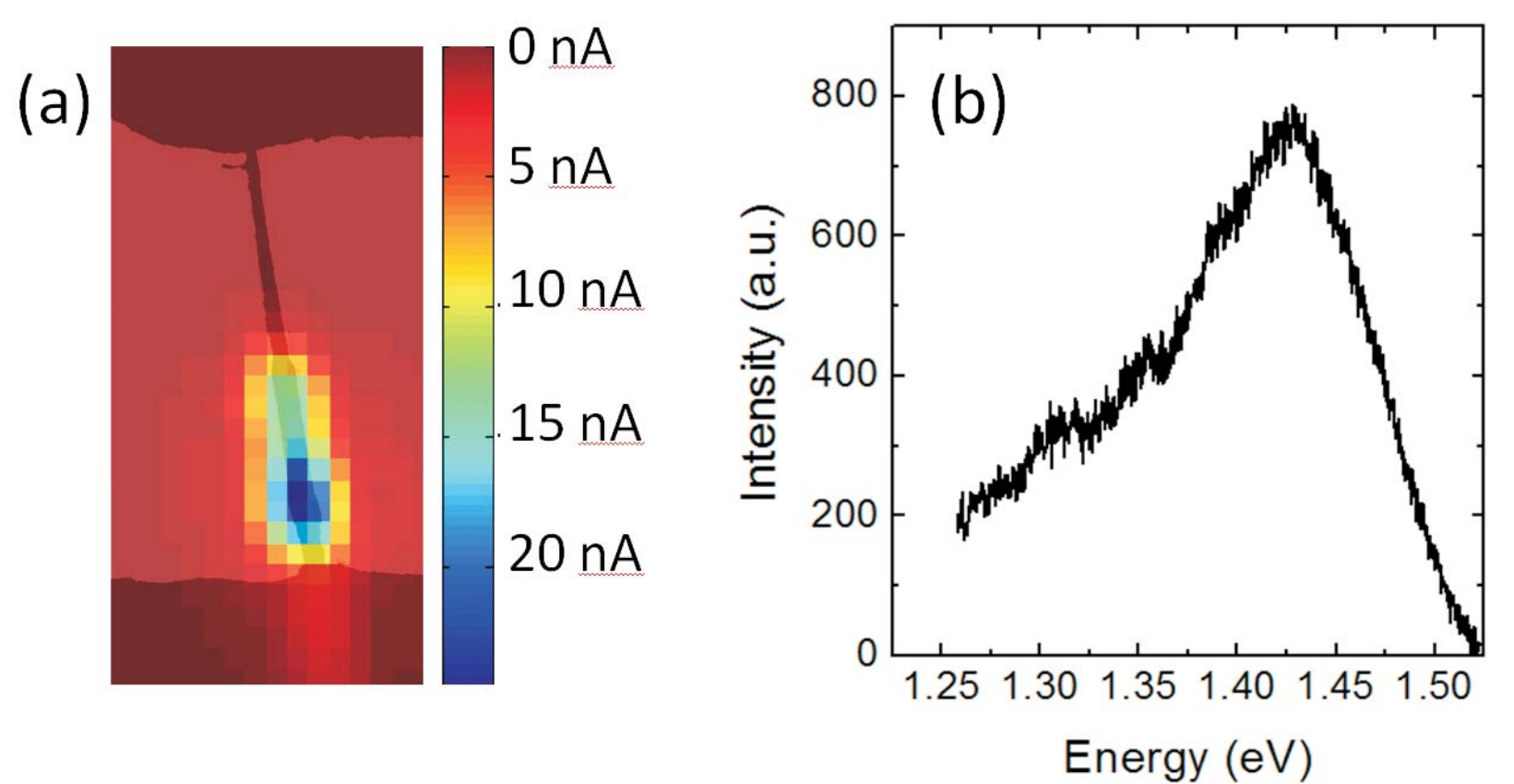
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Energy (eV)